

### DESCRIPTION

## 5

The present invention relates to a method for partially treating a water-repellent glass sheet to remove part of a water-repellent function of the glass sheet. The invention  
10 also relates to a water-repellent glass sheet with part of its water-repellent film removed.

In recent years, water-repellent glass sheets are  
15 widely used on vehicles so as to repel rain drops from  
fields of view of drivers of the vehicles to thereby ensure  
safety driving in a rainy weather.

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desired water-repellent function.

5 Of vehicular glass sheets, a water-repellent pane of glass provided sidewardly of a vehicle has a lower portion connected to a lift mechanism called a window regulator for raising and lowering the pane of glass. More specifically, the water-repellent pane of glass is connected to holders  
10 of metal by means of resin or adhesive applied thereto. The holders are then bolted to arms of the lift mechanism. The holder can be readily adhered to a laminated glass pane or another glass pane free from a water-repellent function. However, a problem is encountered in connecting the holders  
15 to a water-repellent pane of glass by means of an adhesive. More specifically, it is impossible to achieve a required adhesive strength between the adhesive and the glass pane because the water-repellent film of the water-repellent pane of glass functions to repel the adhesive. As a  
20 consequence, the holders cannot be attached to the water-repellent glass pane. To overcome this problem, either abrasives (abrasive method) or masking tapes (masking tape method) have been conventionally used.

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the holders through an adhesive applied thereto.

However, in the abrasive method, it is difficult and laborious to partially remove the water-repellent film by means of abrasives, thereby increasing the cost of processing of the water-repellent film.

Reference is now made to FIG. 8 hereof schematically illustrating a conventional front glass pane or windshield. As in some conventional windshields, the illustrated windshield 101 includes wipers 102, 102 movable across the windshield to remove rain, and optical instruments such as a rain sensor 103 for detecting whether any rain drops are present on the windshield, or the amount of the rain drops on the windshield.

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is illustrated in enlarged-scale partial cross section taken along line 9-9 of FIG. 8. The windshield 101 has a water-repellent film 104 formed on an external surface of the windshield 101. The water-repellent function of the film 104 becomes gradually degraded with the lapse of years. In correspondence with the degradation, the states of adherence of rain to the windshield 101 also change. It is quite tedious to make the relevant control follow those changes. In the light of the tedious adjustments thus required of the control to follow the changes, the front glass pane 101 may as well go without the water-repellent film 104.

To this end, one may propose to provide a small window-shaped water-repellent-film-free part 105 so that the rain sensor 103 can be mounted to the windshield 101 in opposed relation to the film-free part 105. This arrangement enables automatic wiping wherein the wipers 102, 102 are automatically operated in correspondence with the amount of rain present on the film-free or non-repellent part 105 of the windshield 101. It also becomes possible to urge, by signals, or phonetic or optical means, a driver to start the wipers.

Incidentally, for prolonging the life of the water-repellent film 104, it is desirable to provide a relatively thick ground film or undercoat of  $\text{SiO}_2$  interposed between the water-repellent film 104 and the front glass pane 101.

Now, the non-repellent part 105 may be formed in the water-repellent film 104 and the ground film laid thereunder by using either the abrasive method or the masking tape method. However, since the water-repellent

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Reference is made next to FIG. 10 which schematically illustrates interrelations between a conventional door glass pane and a conventional door mirror. A driver, not shown but seated in a driver seat 111 with his hands held onto a steering wheel 112, looks into the door mirror 115 through the door glass pane 114 for rearward confirmation.

As can be readily appreciated, the water-repellent part 117 is surrounded by a non-water-repellent part 118 of the door glass pane 114. When the non-water-repellent part 118 is provided by means of the abrasive method or the masking tape method, an edge 119 of the water-repellent part 117 lies normal to a surface of the door glass pane 114. Then, it is likely that the edge 119, when shone with rays of

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light from a succeeding car or a passing-by car, or with roadside lights, undesirably serves as a reflecting surface and shines to thereby block the driver's rear view. In this instance, the water-repellent part 117 loses its  
5 significance of being provided.

## DISCLOSURE OF THE INVENTION

It is accordingly an object of the present invention to provide a method for removing part of a water-repellent  
10 film formed on a glass sheet, without using abrasives and/or masking tapes.

Another object of the present invention is to provide a water-repellent sheet of glass free from the foregoing optical inconveniences.

15 To attain the above objects, there is provided, in accordance with one aspect of the present invention, a method for partially treating a water-repellent glass sheet to remove part of a water-repellent function of the glass sheet, which method comprises the steps of: providing a  
20 glass sheet having a water-repellent film formed thereon; and irradiating a desired part of the water-repellent film with a stream of plasma jets to thereby eliminate the desired film part.

Since the plasma jet stream is limited in its radial  
25 expansion and narrower than a gas flame, it is possible to treat a desired portion of the water-repellent film precisely. The plasma jet irradiation may be effected by moving a plasma jet irradiation gun relative to and along a surface of the water-repellent film. Since such movement  
30 of the plasma jet irradiation gun can be achieved with no

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In a preferred form, the water-repellent glass sheet  
5 includes an  $\text{SiO}_2$ -based undercoat interposed between a  
surface of the glass sheet and the water-repellent film.  
The desired-film-part elimination may be carried out such  
that the undercoat is left as it is.

15 Preferably, the plasma jet irradiating step is  
performed by using a plasma jet irradiation gun which is  
set to operate at a power output of the order of 0.5 kW, is  
positioned 5-15 mm distant from the glass sheet and is set  
to move at a velocity of 1-60 mm/sec parallel to a surface  
20 of the glass sheet in each pass of treatment.

The term "conversion velocity" used herein represents a rate obtained when a velocity of movement of the plasma jet irradiation gun parallel to the surface of the water-repellent glass sheet is divided by the number of times the

water-repellent glass sheet is treated with plasma jets. The conversion velocity is set to be 1 mm/sec or more, preferably 10 mm/sec or more, and more preferably 20 mm/sec or more while the conversion velocity is set to be 60

5 mm/sec or less, preferably 50 mm/sec or less, and more preferably 40 mm/sec or less. By using these parameters, a stable plasma jet stream is provided to thereby efficiently remove a desired part of the water-repellent film.

According to another aspect of the present invention,  
10 there is provided a water-repellent glass sheet produced by  
the partial treatment method described above. The glass  
sheet may be a curved one because it is treated by the  
plasma jets which achieve precise treatment.

According to a further aspect of the present invention, there is provided a water-repellent glass sheet which comprises an  $\text{SiO}_2$ -based undercoat formed on a surface of said glass sheet; and a water-repellent film formed on the undercoat. The water-repellent film has non-water-repellent portions provided by nullifying a water-repellent function at portions thereof where a water-repellent function is not required, and a sloped border portion separating the non-water-repellent portions and remaining water-repellent portion. The sloped border portion has a gradient water-repellent function.

25       At the sloped border portion where the water-repellent  
function is gradient, the thickness of the water-repellent  
film decreases gradually from 10% to 0%. As a result,  
undesirable shining of the border portion and mis-operation  
of a rain sensor disposed inside a car, which are caused by  
30 rays of light of a passing-by car shining onto the border



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portion and the sensor, can be prevented.

It is desirable that the undercoat remains present at the non-water-repellent portions. With the undercoat kept present at those portions, no large stepped portion will be  
5 formed thereat, whereby optical problems due to light reflection, otherwise occurring at those portions, can be avoided.

The undercoat may be formed by a sol-gel process which enables film forming at a low-temperature atmosphere. This  
10 leads to increased productivity and hence reduction in the cost of production.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Certain preferred embodiments of the present invention  
15 will hereinafter be described in detail, by way of example only, with reference to the accompanying drawings, in which:

FIG. 1 is a front elevational view of a plasma jet irradiation gun for use in a method according to the  
20 present invention;

FIG. 2 is a cross-sectional view taken along line 2-2 of FIG. 1;

FIG. 3A illustrates how a water-repellent glass sheet is irradiated with plasma jets by use of the plasma jet  
25 irradiation gun;

FIG. 3B is a graphical illustration of the treatment capability of the plasma jets;

FIG. 4A is a cross-sectional view illustrating the water-repellent glass sheet to be irradiated with plasma  
30 jets;

FIG. 4B is a diagrammatic illustration of the molecular structure of the water-repellent film;

5        FIG. 5B is a cross-sectional view illustrating the water-repellent film with part eliminated as a result of the irradiation with the plasma jets:

10        FIGS. 7A and 7B illustrate the principles of tension  
and peeling tests for measuring the adhesive strength  
between glass sheets and adhesives.

15       The following description is merely exemplary in nature  
and is in no way intended to limit the invention or its  
application or uses.

As shown in FIG. 2, an air fan 20 is positioned backwardly of the blower mount block 13. The air fan 20 includes a motor 21, blades 23 attached to a motor shaft 22, a spiral casing 24 wound around the blades 23, an air intake aperture 25, and a net 26. An electrode rod 30 and an electrode board 31 are provided forwardly of the air fan 20. The electrode board 31 faces toward the flow path 11.

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produced therebetween. At the same time, the air fan 20 causes air to flow along the flow path 11 at a high velocity, thereby generating a high-speed stream of plasma jets 33. The plasma jets 33 are discharged through the nozzle 14. The plasma jets 33 having a high velocity can hardly expand radially and thus flow in a generally linear stream.

Next, reference is made to FIG. 4A illustrating, in  
20 cross-section, the construction of a water-repellent glass  
sheet to be treated by the method according to the present  
invention.

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Reference is now made to FIGS. 5A and 5B illustrating the partial treatment method according to the present invention. The plasma jet irradiation gun 10 irradiates the water-repellent film 43 with the plasma jets 33, as shown in FIG. 5A, whereupon a reaction as described below is brought about by the energy of the plasma jets 33.

Each bond between silicon and carbon, indicated by horizontally directed arrows in FIG. 4B, is primarily broken, whereby the water-repellent function is eliminated.

As shown in FIG. 5B, the water-repellent glass sheet 40 includes a portion directly irradiated with the plasma jets 33 in such a manner as to remove the water-repellent film 43 having the water-repellent function. More specifically, 20 fluorine-containing groups having the water-repellent function are eliminated by the plasma jets. Such a portion free from the water-repellent film 43 is hereinafter referred to as "non-water-repellent portion". The water-repellent glass sheet 40 also includes a "water-repellent 25 portion" not irradiated with the plasma jets 33. The water-repellent portion has the water-repellent film 43 left unremoved. Between the non-water-repellent portion and the water-repellent portion, there is provided a "border portion". The border portion gradually decreases 30 in irradiance towards the water-repellent portion to

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thereby provide an inclined or sloped surface.

### EXPERIMENTS

Experiments in the present invention will be discussed  
5 below. However, the present invention is not limited to  
the experiments to be described below. The plasma jet  
irradiation gun 10 moves in parallel to the surface of the  
water-repellent glass sheet 40 when the water-repellent  
glass sheet 40 is treated with plasma jets.

#### 10 EXAMPLE 1

EXPERIMENTAL EQUIPMENT: APPARATUS FOR TREATING FORMED  
PRODUCT WITH PLASMA JETS (available from  
COROTEC Corp.)

15 SAMPLE: water-repellent glass sheet (including an  
undercoat of  $\text{SiO}_2$  having a thickness of 40 nm, and a  
water-repellent film of perfluoroalkylsilane  
having a thickness of 4 nm)

DISTANCE H: 10 mm (See FIG. 3A)

POWER: 0.5 kW for each plasma jet irradiation gun  
20 STRIKING VELOCITY OF PLASMA JETS (rate at which plasma  
jets impact upon a sample): about 7 m/s

VELOCITY OF PLASMA JET IRRADIATION GUN (in movement  
parallel to the water-repellent glass sheet  
surface); 100 mm/sec

25 TREATMENT: two times

CONVERSION VELOCITY: 50 mm/sec

EVALUATION: contact angle

FIG. 6 is a graph showing contact angles obtained from  
30 EXAMPLE 1. A horizontal axis shows the distance L (See

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FIG. 3B) from the center of the surface of the water-repellent glass sheet irradiated with plasma jets. A vertical axis shows contact angles  $\theta$ . A contact angle  $\theta$  is given between the surface of the water-repellent glass sheet and the surface of a drip or raindrop placed on the former. The contact angle is important in determining the water-repellent function of the water-repellent glass sheet. The greater the contact angles  $\theta$  are, the higher the water-repellent function becomes. In the graph, the contact angle  $\theta_1$  is about  $110^\circ$  to provide a "water-repellent state" in which water is repelled.

Contact angle  $\theta_2$  is about  $10^\circ$  in which angle a rain-drop takes a flattened shape and adheres to the water-repellent glass sheet with increased firmness. This state may be called "wettability". When wettability is high, it is unlikely that a primer or an adhesive agent is repelled. Then, holders can be fixedly attached to the glass sheet with a minimum of difficulty.

#### EXAMPLES 2 to 4

20      **EXPERIMENTAL EQUIPMENT: APPARATUS FOR TREATING FORMED PRODUCT WITH PLASMA JETS** (available from COROTEC Corp.)

25      **SAMPLE: water-repellent glass sheet** (including an undercoat of  $\text{SiO}_2$  having a thickness of 30 to 40 nm, and a water-repellent film of perfluoroalkylsilane having a thickness of 2 to 5 nm)

**DISTANCE H: 10 mm**

**POWER: 0.5 kW for each plasma jet irradiation gun**

**STRIKING VELOCITY OF PLASMA JET: about 7 m/s**

30      **VELOCITY OF PLASMA JET IRRADIATION GUN: 100, 20, and**



In EXAMPLE 4, the water-repellent glass sheet is treated with the plasma jet irradiation gun having a high velocity of 120 mm/s. The water-repellent glass sheet is treated once. The conversion velocity is 120 mm/s. Consequently, a contact angle varies and hence the desired contact angle can not be achieved. For this reason, the evaluation is no good.

Figs. 7A and 7B illustrate the principles of tension  
15 and peeling tests for measuring the adhesive strength  
between glass sheets and adhesives.

Turning to FIG. 7B, a ribbon 47 includes a portion adhered to the glass sheet 41 and having a width of 25 mm. The ribbon 47 is then peeled off the glass sheet 47 by a force  $F_z$  applied thereto, as shown in FIG. 7B. Such a  
30 force  $F_z$  is the adhesive strength in the peeling test.



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EXAMPLES 5 to 7

EXPERIMENTAL EQUIPMENT: APPARATUS FOR TREATING FORMED  
PRODUCT WITH PLASMA JET (available from COROTEC  
Corp.)

- 5 SAMPLE: water-repellent glass sheet (including an  
undercoat of  $\text{SiO}_2$  having a thickness of 30 to 40 nm,  
and a water-repellent film of perfluoroalkylsilane  
having a thickness of 2 to 5 nm) or a conventional  
glass sheet
- 10 DISTANCE H: 10 mm  
POWER: 0.5 kW for each plasma jet irradiation gun  
STRIKING VELOCITY OF PLASMA JET: about 7 m/s  
VELOCITY OF PLASMA JET IRRADIATION GUN: 40 mm/sec  
TREATMENT: twice
- 15 CONVERSION VELOCITY: 20 mm/sec

TABLE 2

	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7
Distance H	10 mm	10 mm	10 mm
20 Velocity of Plasma Jet Irradiation Gun	40 mm/s	40 mm/s	40 mm/s
Treatment	twice	twice	twice
Conversion Velocity	20 mm/s	20 mm/s	20 mm/s
Tested Portion	non-water-repellent portion	water-repellent portion	surface of conventional glass sheet
25 Adhesive Strength Fx	80 kgf	0	59 kgf

Adhesive Strength FZ	10 kgf or more	0	10 kgf or more
Failure	cohesive failure	interfacial failure	cohesive failure

In EXAMPLE 6, the water-repellent portion of the water-repellent glass sheet is tested. The adhesive strength  $F_x$  in the tension test and the adhesive strength  $F_z$  in the peeling test are both zero, and interfacial failure occurred at the water-repellent portion. This means that because the water-repellent portion repels adhesive, the glass sheets 41, 41 can not be bonded together while the ribbon 47 can not be bonded to the glass sheet 41.

Further, the previously stated experiments were performed repeatedly. Results obtained from those

experiments show that the present invention can be carried out when the distance H is in the range of 5 to 15 mm. The distance H of less than 5 mm provides unstable plasma jet. When the distance H is more than 15 mm, plasma jet is too long. Therefore, the distance H is preferably set to be 5 mm or more and be up to 15 mm. The power is set to be between 0.3 and 1 kW.

### EXAMPLES 8 to 16

**SAMPLE:** a water-repellent glass sheet (including an undercoat of  $\text{SiO}_2$  having a thickness of 30 to 40 nm. and a water-repellent film of perfluoroalkylsilane having a thickness of 2 to 5 nm)

POWER: 0.5 kW for each plasma jet irradiation gun

**STRIKING VELOCITY OF PLASMA JET:** about 7 m/s

**VELOCITY OF PLASMA JET IRRADIATION GUN: 0.5 to 70 mm/s**

**25            TREATMENT: once**

TABLE 3

	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16
Distance H (mm)	10	10	10	10	10	10	10	10	10
Velocity of Plasma Jet	0.5	1.0	10	20	30	40	50	60	70
Irradiation Gun (mm/s)									
Frequency of Treatment	once	once	once	once	once	once	once	once	once
Conversion Velocity (mm/s)	0.5	1.0	10	20	30	40	50	60	70
Evaluation on Treatment	Very Good	Very Good	Very Good	Very Good	Very Good	Very Good	Good	Fair	No Good
Evaluation on Cost Efficiency	No Good	Fair	Good	Very Good	Very Good	Very Good	Very Good	Very Good	Very Good
Total Evaluation	No Good	Fair	Good	Very Good	Very Good	Very Good	Good	Fair	No Good

In EXAMPLE 9, the conversion velocity is 1.0 mm/sec. The water-repellent film was satisfactorily eliminated to thereby obtain an evaluation of very good on the treatment.

15 The plasma jet irradiation gun in EXAMPLE 9 moves twice faster than that in EXAMPLE 8. Therefore, the number of the non-water-repellent portions produced in EXAMPLE 9 is twice that in EXAMPLE 8. Thus, the cost efficiency is fair in evaluation. Thus, the total evaluation on EXAMPLE 9 is

20 fair.

In EXAMPLE 10, the conversion velocity is 10 mm/sec. The water-repellent film was satisfactorily eliminated to thereby obtain a very good evaluation on the treatment. The plasma jet irradiation gun in EXAMPLE 10 moves much  
25 faster than that in EXAMPLE 9 to thereby obtain a good evaluation on the cost efficiency. The total evaluation on EXAMPLE 10 is therefore good.

In EXAMPLE 11, the conversion velocity is 20 mm/sec. The water-repellent film was satisfactorily eliminated to  
30 thereby obtain a very good evaluation on the treatment.

The velocity of the plasma jet irradiation gun in EXAMPLE 11 is much greater than that in EXAMPLE 10 to thereby obtain an evaluation of very good on the cost efficiency. Therefore, the total evaluation on EXAMPLE 11 is very good.

In EXAMPLE 13, the conversion velocity is 40 mm/sec. The water-repellent film was satisfactorily eliminated to thereby obtain a very good evaluation on the treatment.

In EXAMPLE 14, the conversion velocity is 50 mm/sec. The velocity of the plasma jet irradiation gun in EXAMPLE 14 is greater than that in EXAMPLE 13 to thereby obtain an evaluation of very good on the cost efficiency. However, since the velocity of the plasma jet irradiation gun in EXAMPLE 14 is higher than that in EXAMPLE 13, the water-repellent film was removed to a smaller extent in EXAMPLE 14 than in EXAMPLE 13. Thus, the evaluation on the treatment is good to thereby obtain a total evaluation of good.

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greater than that in EXAMPLE 14 to thereby obtain a very good evaluation on the cost efficiency. However, since the plasma jet irradiation gun in EXAMPLE 15 has a much greater velocity than that in EXAMPLE 14, the water-repellent film was removed to a smaller extent in EXAMPLE 15 than in EXAMPLE 14. The conversion velocity in EXAMPLE 15 is an upper limit for obtaining a fair evaluation on the treatment. The total evaluation on EXAMPLE 15 is thus fair because the evaluation on the treatment is fair.

The results of the experiments in EXAMPLES 8 to 16 show that the conversion velocity should be 1 mm/sec or more, preferably 10 mm/sec or more, and more preferably 20 mm/sec or more while the conversion velocity should be 60 mm/sec or less, preferably 50 mm/sec or less, and more preferably 40 mm/sec or less.

30

$$\text{A} - \left[ \begin{array}{c} \text{CH}_3 \\ | \\ (\text{SiO}) \\ | \\ \text{CH}_3 \end{array} \right]_n - \text{A} \quad \text{.....Compound 1}$$

10

$$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \quad \quad \text{CH}_3 \\ | \quad \quad | \quad \quad | \\ (\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2-(\text{SiO})_m-(\text{SiO})_n-\text{SiCH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \quad \text{Compound 2} \\ | \quad \quad | \quad \quad | \\ \text{CH}_3 \quad \quad \text{OSi}(\text{OCH}_3)_3 \quad \text{CH}_3 \end{array}$$

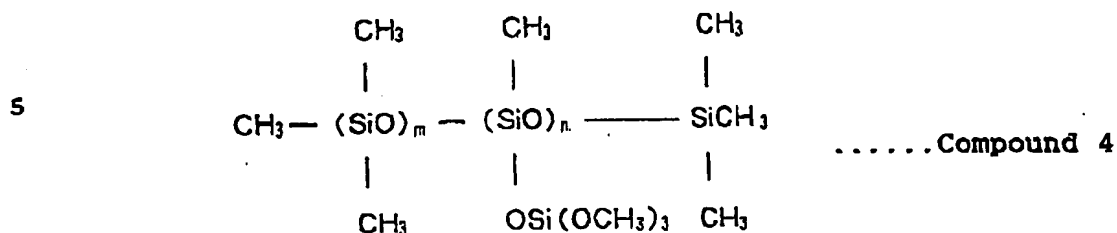
20

$$\begin{array}{ccccccc}
 & \text{CH}_3 & & \text{CH}_3 & & & \text{CH}_3 \\
 & | & & | & & & | \\
 \text{CH}_3 - & (\text{SiO})_m - & (\text{SiO})_n - & & \text{SiOSi}(\text{OCH}_3)_3 & \dots\dots\text{Compound 3} \\
 & | & & | & & & | \\
 & \text{CH}_3 & & \text{OSi}(\text{OCH}_3)_3 & & & \text{CH}_3
 \end{array}$$

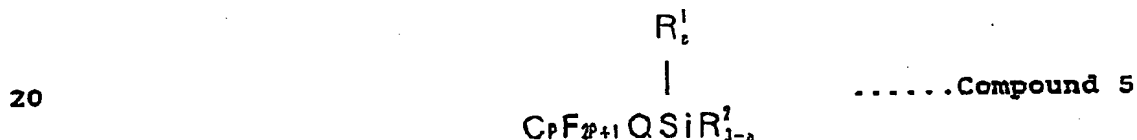
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where m denotes an integer in the range of 3 to 100, n is an integer between 0 and 50, and m+n is 3 or more and up to 30 100 and preferably 10 or more and up to 50.





The water-repellent films obtained using the previously described compounds 1 through 4 do not contain fluorine but have a capability of repelling water. Such water-repellent films could be effectively treated in accordance with the present invention.



Although the compact and useful plasma jet irradiation  
30 gun 10 is employed in the embodiment of the present

invention, the construction of the plasma jet irradiation gun is not limited to that described in relation to FIGS. 1 and 2 as long as a device for generating plasma jets is employed.

5

As thus far explained, in accordance with the present invention, part of a water-repellent function or film of a water-repellent glass sheet can be removed easily by means of plasma jets. As a result, when the water-repellent glass sheet is used as an automobile door glass pane, holders of a window regulator for raising and lowering the door glass pane can be attached with increased firmness to the non-water-repellent part of the glass pane by means of an adhesive because the adhesive is no longer repelled.

Also, when the glass sheet with the water-repellent-  
25 film-free part is used as a windshield of a vehicle, a rain  
sensor can be mounted to the windshield in opposed relation  
to the water-repellent-film-free part. As a result, the  
rain sensor can surely detect rain because rain fell on the  
water-repellent-film-free part is not repelled and stays  
30 there for detection. This further enables the provision of

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an automatic wiping system.

Although the glass sheet treated in accordance with the present invention has been described in relation to use on and application to an automobile, it should not be limited 5 to such use and application. For example, the inventive glass sheet can also be applied to trains, airplanes, boats and other means of transportation employing sheets of glass.